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BRIGHT DIP

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4 Claims. (Cl. 148—8)

This invention relates to bright-dips for zinc plated articles, and is particularly directed to bright-dips, and to processes of bright-dipping, which employ acidic or basic solutions of oxidizing agents such as hydrogen peroxide, nitric acid, and the like.

In addition to their low cost, electrodeposited zinc coatings display many characteristics which should cause them to be particularly desirable as protective and ornamental finishes. Although zinc is not itself very resistant to corrosion, it does not accelerate the corrosion of iron or steel as do such metals as copper and nickel. On the contrary, zinc being higher in the electromotive series, will protect iron or steel against rusting even after appreciable areas of the base metal are exposed. Polished zinc metal, moreover, has a pleasing metallic lustre with a slightly blue hue.

Despite their numerous advantages over many commonly used coating materials, electrodeposited zinc coatings have not enjoyed the use which they deserve because they do not possess, and even if polished, do not retain a pleasing appearance. The known methods of electroplating zinc almost invariably result in dark, discolored plates. Even when the plates at first have a fairly satisfactory appearance, they soon become dark and discolored. Moreover, the electrodeposited zins coatings are very susceptible to staining: for instance, when they are touched with the fingers in handling, they are marked and stained by the mere contact.

I have found that the treatment of electrodeposited zinc coatings with an acidic or basic oxidizing solution, particularly with an acidic hydrogen peroxide solution, produces a desirably bright and lustrous finish. This finish displays a passivity to staining, and it may be handled without danger to its appearance. The finish, moreover, is much more resistant to corrosion and tarnishing than zinc coatings which have not been bright-dipped. At a low cost I thus obtain a finish that is acceptable in practically any field which requires a protective metallic finish.

The bright dips of this invention are characterized by the presence of an oxidizing agent in a solution having a pH above or below 7. In other words, they are oxidizing solutions which contain an excess of one of the ions of water. Ordinarily the pH is adjusted by adding an acidic or basic material to the solution. In high concentration, these acidic and basic materials exhibit the property of etching zinc, and I may, accordingly, term them etching agents. It will be apparent that while I call these materials etching agents, it is not their etching effect which I utilize. They are used in such small concentrations that no appreciable etching action, as such, is discernible on inspection of the zinc after treatment.

Neither the oxidizing agents nor the etching agents serve alone as a satisfactory bright-dip. Alone the oxidizing agent sometimes removes a slight amount of stain, and alone the etching agent, in the small concentrations used, has little effect.

The ratio of oxidizing agent to etching agent is of great importance. There must not be so much etching agent present that the zinc will be etched before a satisfactory brightening is obtained. It is a relatively easy matter empirically to determine a satisfactory ratio by adding to water a quantity of oxidizing agent, and then adding a very small amount of an etching agent. If a satisfactory finish is not obtained on dipping a freshly plated sample, more etching agent is added until a satisfactory finish is obtained. Care must be exercised lest too much etching agent be added. The addition of an excessive amount of etching agent is indicated by an etching of the finish.

After a dip has been made up according to the above method, it may be that it acts too slowly or too rapidly. If the action is too slow, more of the oxidizing and etching agents should be added; while if the action is too rapid, the dip should be diluted with water.

The bright-dip compositions of this invention are characterized by the presence of an oxidizing agent and such a quantity of an etching agent that the combined effect is the production of a satisfactorily bright finish of an electrodeposited zinc coating without the etching agent exercising, in the interval of exposure, a deleterious etching action.

The following specific examples are given more fully to illustrate the practice of my invention:

Example 1.—Pieces of sheet steel 2'' x 6'' were plated in the following solution and operating conditions:

Electrolyte

	Oz./gallon
Zinc cyanide	10
Sodium cyanide	3
Caustic soda	10

The solution was purified by electrolyzing it for 24 hours under the following operating conditions:

Cathode current density	10 amperes per square foot
Anode current density	20° to 30° C.
Bath temperature	5 amperes per square foot

After the purification by electrolysis, the electrolyte was employed under the following conditions:

Bath temperature	20° to 30° C.
Cathode current density	10 to 15 amperes per square foot

Zinc plated articles so obtained were rinsed with water and then subjected to the action of a bright-dip consisting of a 1% aqueous nitric acid solution. The bright-dip was used at room temperature. After about 10 to 30 seconds, the articles were satisfactorily bright, and they were then rinsed with water and dried.

Example 2.—Articles plated as in Example 1 were treated for 10 to 30 seconds at room temperature in a bright-dip consisting of an aqueous solution of:

2 to 5% by weight of sulfuric acid
2 to 5% by weight of 100-volume hydrogen peroxide

Example 3.—Articles plated as in Example 1 were treated at room temperature in a bright-dip consisting of an aqueous solution of:

Sodium cyanide___ 2 to 4 ounces per gal.
Hydrogen peroxide_ (100-vol.) 2 to 5% by weight

Example 4.—An article was plated in known manner in a conventional bath of the following composition:

	Grams per liter
NaOH	38
NaCN	80
ZnO	45
Gelatine	1

The plated article was removed from the bath, and rinsed with water. It was subjected to a bright-dip consisting of an aqueous solution containing:

	Per cent
Sodium nitrate	2
Sodium hydroxide	0.01

The bright-dipped article was then rinsed with water and dried.

Example 5.—An article, zinc plated as in Example 4, was subjected to the action of a bright-dip consisting of an aqueous solution containing:

Sodium Nitrate_____ 2% by weight
Concentrated nitric acid_____ 2 cc. per liter

Better results were obtained than in Example 4.

Example 6.—An article, zinc plated as in Example 4, was subjected to the action of a bright-dip consisting of an aqueous solution containing:

	Per cent
Sodium chlorate	2
Sulfuric acid	0.25

Example 7.—An article, zinc plated as in Example 4, was subjected to the action of a bright-dip consisting of an aqueous solution containing:

	Per cent
Sodium chlorate	2
Sodium hydroxide	1

While I have mentioned specific types of plating baths as in the examples, I do not intend to be limited thereby. I may use my bright-dips on articles plated by any method. In general, however, the most satisfactory results are achieved when as smooth and clean a plated example as is obtainable is treated. When, for example, an articles is plated in a sulfate bath without an addition agent, the plate is very rough and discolored. I then must use a greater ratio of acid or alkali to oxidizing agent in order to obtain even a relatively smooth finish, and even then the final plate is not as saisfactory as when more improved plating methods are used.

It is noted that sulfate baths with suitable addition agents and/or brightening agents yield a more satisfactory finish, and electrodeposited zinc coatings from such baths may, of course, be advantageously treated according to my invention.

While I have given specific proportions in my examples, I do not intend to be limited thereto. The exact proportion and amount of ingredients for my bright-dips vary with the bath used, the manner of use, and numerous other conditions met with in practice. The optimum formulation under a given set of conditions is readily determinable according to the methods hitherto outlined. It is noted that in any case the quantities are not critical and fair results may be obtained over a rather extended range.

Instead of the oxidizing agents heretofore mentioned, I may use others such as sodium persulfate, ammonium persulfate, sodium permanganate, sodium peroxide, barium permanganate, barium peroxide, soluble chlorates, and soluble perchlorates.

I may use any suitable etching agent with the oxidizing agent. Some oxidizing agents are themselves acidic or basic in their nature and do not require the addition of an etching agent. Nitric acid, for instance, acts both as an acid, lowering the pH of the solution, and as an oxidizing agent. Great care must be exercised in the use of these acidic or basic oxidizing agents lest their concentration be so great as to cause a deleterious etching action. Some basic or acidic oxidizing agents are so weakly basic or acidic that it is necessary to supplement them with additional base or acid. It may sometimes be desirable to so supplement even rather strongly basic or acidic oxidizing agents.

It is, of course, apparent that when selecting an etching agent for use with a particular oxidizing agent, care must be taken lest they react. For instance, sodium perborate would preferably be used with an alkaline etching agent.

It will be readily apparent that I may use various acidic or basic materials other than those listed in the above examples. I may, for instance, use acids such as hydrochloric acid, phosphoric acid, carbonic acid, acetic acid, and lactic acid. Very weak acids such as carbonic acid and hypochlorous acid are none too satisfactory for, while they operate as do stronger acids, they are effective to a much smaller degree. Some acids, such as hydriodic acid, are not economical when used with hydrogen peroxide because they cause a rather rapid decomposition of the peroxide. While I may use any acid, organic or inorganic, I prefer to use acetic acid or a mineral acid such as sulfuric acid or hydrochloric acid.

Instead of using acids, I may use acidulous salts such as ferric chloride, potassium per sulfate, and sodium bisulfate.

Instead of the acidic etching agent above mentioned, I may use such basic materials as potassium hydroxide, ammonium hydroxide, and sodium carbonate. Ordinarily, I do not prefer to employ basic materials, and especially not with hydrogen peroxide. Most basic materials accelerate the decomposition of hydrogen peroxide and thus shorten the life of the bright-dip.

It is noted that, generally speaking, neither the etching agent nor oxidizing agent should contain a compound the cation of which is a metal below zinc in the electromotive series. If such a compound be present in the bright-dip, the metal, being below zinc in the electromotive force series, will be deposited on the zinc. The deposited

metal usually mars the appearance of the zinc finish.

While, as above noted, I may use any oxidizing agent with a suitable acidic or basic material, I prefer to use acidic solutions of hydrogen peroxide. Hydrogen peroxide acidified with sulfuric acid has given by far the best results with zinc plates electrodeposited by various methods.

While I have shown numerous specific compositions and processes, I do not intend to be limited thereto, the scope of my invention appearing from the following claims:

This application is a continuation in part of my application Serial No. 752,703, and 752,704, filed Nov. 12, 1934, which issued Mar. 30, 1937 as U. S. Patent No. 2,075,623.

I claim:

1. In a process of bright-dipping and passivating an electrodeposited zinc coating, the step comprising subjecting the zinc to the action of an acidic solution of hydrogen peroxide the duration of the treatment being so adjusted that the zinc surface is brightened without deleterious etching.

2. The process comprising subjecting an electroplated zinc surface to the action of a dilute, acidic, aqueous solution of hydrogen peroxide containing about 2 to 5% by weight of sulfuric acid, until said zinc surface is brightened and removing said surface from the action of said solution before said surface becomes etched to such an extent as would appreciably diminish the brightening effect.

3. A method of treating zinc to brighten the same, comprising subjecting the zinc to the action of an acidified solution of hydrogen peroxide having a limited excess of H_2O_2 over that required by the equation $Zn+2H^++H_2O_2=Zn^{++}+2H_2O$.

4. A method of treating zinc to brighten the same, comprising subjecting the zinc to the action of a solution of hydrogen peroxide and sulfuric acid having a limited excess of H_2O_2 over that required by the equation

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CERTIFICATE OF CORRECTION.

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows: Page 1, first column, line 30, for "zins" read zinc; same page, second column, lines 51 to 53, for

"Anode current density___ 20° to 30° C.
Bath temperature_____ 5 amperes per square foot"

read

Anode current density___ 5 amperes per square foot
Bath temperature_____ 20° to 30° C. ;

page 2, first column, lines 34, 51, and 58, Examples 4, 6, and 7 respectively, after the words "Per cent" insert by weight; line 67, for "example" read article; page 3, first column, line 14, for "application" read applications; and that the said Letters Patent should be read with this correction therein that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 15th day of August, A. D. 1939.

Leslie Frazer

(Seal) Acting Commissioner of Patents.

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